

## Photoacoustic Thermal Characterization of Porous Rare-Earth Phosphate Ceramics

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*Received: May 18, 2006*

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The laser induced non-destructive photoacoustic technique has been employed to measure the thermal diffusivity of lanthanum phosphate ceramics prepared by the sol-gel route. The thermal diffusivity value was evaluated by knowing the transition frequency between the thermally thin to thermally thick region from the log-log plot of photoacoustic amplitude versus chopping frequency. Analysis of the data was carried out on the basis of the one-dimensional model of Rosencwaig and Gersho. The present investigation reveals that the sintering temperature has great influence on the propagation of heat carriers and hence on the thermal diffusivity value. The results were interpreted in terms of variations in porosity with sintering temperature as well as with changes in grain size.

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**KEY WORDS:** photoacoustic; porosity; rare-earth phosphate ceramics; thermal diffusivity.

### 1. INTRODUCTION

Rare-earth phosphate ceramics are well-known for their thermal phase stability, high melting point (above 1900°C), excellent resistance to corrosion and irradiation [1], and mechanical properties [2,3], and these materials

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constitute precursors for the further development of thin films and coatings for porous ceramic substrates and composites [4]. However, the performance of the devices based on these materials is essentially determined by their thermal properties such as specific heat capacity [5], thermal diffusivity [6], thermal conductivity, thermal expansion coefficient, etc. In recent years, photoacoustic and related photothermal techniques based on thermal-wave physics have gained wide popularity in measuring thermo-optical properties of materials [7,8], particularly the thermal diffusivity [9,10].

As reported earlier, the diffusion of heat through the ceramics, and hence the thermal diffusivity value, are greatly affected by the pores in the specimen [11], which can be measured using photothermal techniques [12]. In this work, evaluation of the thermal diffusivity of sol-gel derived  $\text{LaPO}_4$  ceramics sintered at different temperatures and a detailed study on the influence of porosity and grain size on the thermal diffusivity value are presented, which are of both scientific and practical significance.

## 2. PREPARATION OF SAMPLE

Lanthanum phosphate was prepared by the sol-gel route using lanthanum nitrate, 99.9% pure (M/s Indian Rare Earths Ltd., India) and orthophosphoric acid (88%, Qualigens Fine Chemicals, India) as starting materials. A 0.07 M solution of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was prepared in water and continuously stirred for 30 min using a mechanical stirrer. A total of 2.394 mL of orthophosphoric acid solution was added slowly to this lanthanum nitrate solution, which yielded a white precipitate of lanthanum phosphate. This precipitate solution was vigorously stirred, and the pH was maintained at 2.2. After 8 h stirring, the lanthanum phosphate precursor sol was obtained. The above precursor sol was maintained for 2 days in an atmosphere of ammonia for aging. The gel of lanthanum phosphate was dried and calcined at  $400^\circ\text{C}$ . The calcined powder was compacted at a pressure of 200 MPa to pellets of 11 mm diameter and 2 mm thickness which were sintered in the range  $800\text{--}1700^\circ\text{C}$ , at a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$  and soaked for 3 h. The thickness of the sample is further reduced to  $\sim 400\ \mu\text{m}$  for the present studies. The relative density of the lanthanum phosphate sample sintered at different temperatures has been measured using an Archimedes displacement method. The porosity  $p$  of specimens having a relative density ' $x$ ' is evaluated to be  $p = 1 - x$ , and those values for samples used in the present investigation, with an error of  $\sim 0.2\%$ , are reported in Table I.

Phase identification of the calcined powders was done by XRD (Phillips PW 1710) in the range  $20\text{--}60^\circ$  using  $\text{CuK}\alpha$  radiation, and the

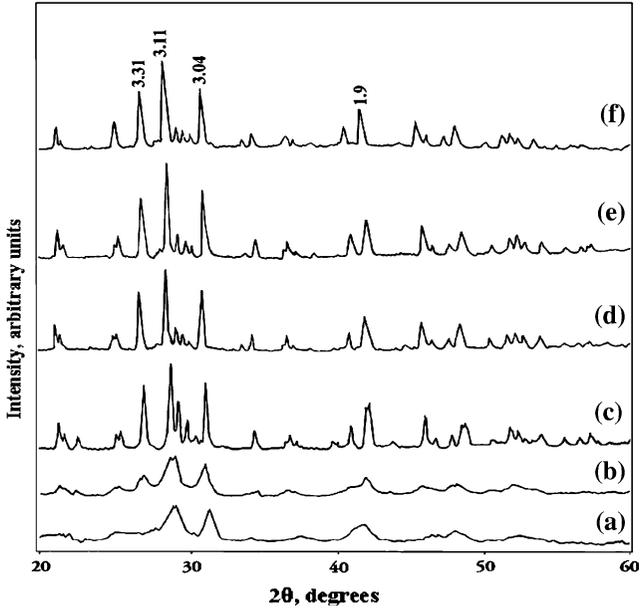
**Table I.** Thermal Diffusivity Values of LaPO<sub>4</sub> Samples

Sintered Temperature (°C)	Porosity (%)	Thermal diffusivity (cm <sup>2</sup> ·s <sup>-1</sup> )	Calculated value of thermal diffusivity (cm <sup>2</sup> ·s <sup>-1</sup> )
800	46	0.176 ± 0.04	0.172
900	39	0.382 ± 0.06	0.388
1100	29.8	0.612 ± 0.06	0.609
1200	10.4	0.920 ± 0.04	0.922
1300	2	1.012 ± 0.05	1.019
1400	4	0.982 ± 0.05	0.997
1500	9	0.934 ± 0.06	0.939

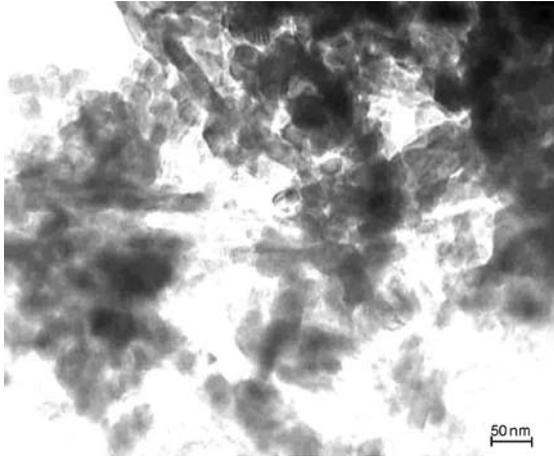
recorded XRD patterns are presented in Fig. 1. The characteristic 'd' values assigned to monazite type LaPO<sub>4</sub> are 3.31, 3.11, 3.04, and 1.9 Å, respectively, according to JCPDS file No: 32 – 0493 and also based on earlier reports [13]. The gel calcined at 400°C showed partial crystallization of LaPO<sub>4</sub>, and that calcined at 800°C showed broad peaks of the LaPO<sub>4</sub> monazite type and phase purity sharp peaks. It is reported that the formation of monazite type CePO<sub>4</sub> from the rhabdophane type occurs above 750°C [14]–[15], similar to that observed in the TEM photograph of the sample under investigation, recorded using JEOL 3000EX (Fig. 2). The polished thermally etched surface of sintered LaPO<sub>4</sub> at 1300 and 1500°C, after providing gold coatings, was observed with a scanning electron microscope (Hitachi, 2240 Japan).

### 3. EXPERIMENTAL SETUP

Continuous optical radiation from an argon ion laser (Liconix 5300) at 488 nm and with a beam diameter of 1.2 mm was used as the source of excitation. The laser beam was irradiated uniformly over the sample surface so that transverse diffusion of heat can be neglected. The beam is mechanically chopped (Stanford Research Systems SR 540) before it impinges on the sample surface. The pressure fluctuations created in the non-resonant PA cell cavity due to the periodic non-radiative de-excitation of the sample is detected using a sensitive microphone (Knowles BT 1754), the output of which is fed to a dual phase lock-in amplifier (Stanford Research Systems SR 830). All the measurements are done at an incident power of 50 mW with a stability of ±0.5%. The theoretical background for the evaluation of the thermal diffusivity from the amplitude spectrum of the PA signal is explained elsewhere [16]. The transition frequency  $f_c$  at which the sample changes from thermally thin (where the



**Fig. 1.** XRD patterns of lanthanum phosphate gels heat different temperatures: (a) 400°C, (b) 800°C, (c) 1100°C, (d) 1400°C (which is 400° C now), (e) 1600°C, and (f) 1700°C.



**Fig. 2.** TEM photograph of the  $\text{LaPO}_4$  ceramics sintered at 800°C.

properties of the backing material determine the PA signal generation which varies as  $f^{-1}$ ) to a thermally thick regime (where the properties of the specimen determine the PA signal generation which varies as  $f^{-1.5}$ ) was obtained from the log-log plot of the PA signal amplitude versus the chopping frequency. The thermal diffusivity value is then evaluated using the expression  $k_c(p) = l_s^2 f_c$ . The experimental setup used for the present investigation is calibrated by evaluating the thermal diffusivity of pure GaAs and Al. The measured values of thermal diffusivity of GaAs and Al ( $0.260 \pm 0.003 \text{ cm}^2 \cdot \text{s}^{-1}$  and  $0.978 \pm 0.004 \text{ cm}^2 \cdot \text{s}^{-1}$ , respectively) agree well with earlier reported values [17,18].

#### 4. RESULTS AND DISCUSSION

The measured thermal diffusivity values of all the lanthanum phosphate gel specimens under investigation are given in Table I. It is obvious that thermal diffusivity values of  $\text{LaPO}_4$  specimens vary with sintering temperature and porosity. A typical variation of PA amplitude spectra for the specimen sintered at  $800^\circ\text{C}$ , characterized by a slope change from  $\sim -1$  to  $-1.5$ , is given in Fig. 3. All other specimens follow similar behavior (not shown here), in accordance with the Rosencwaig and Gersho theory [19]. It is obvious from Table I that the porosity of the ceramic samples decreases with an increase in the sintering temperature up to  $1300^\circ\text{C}$ . Two typical microstructures of thermally etched lanthanum

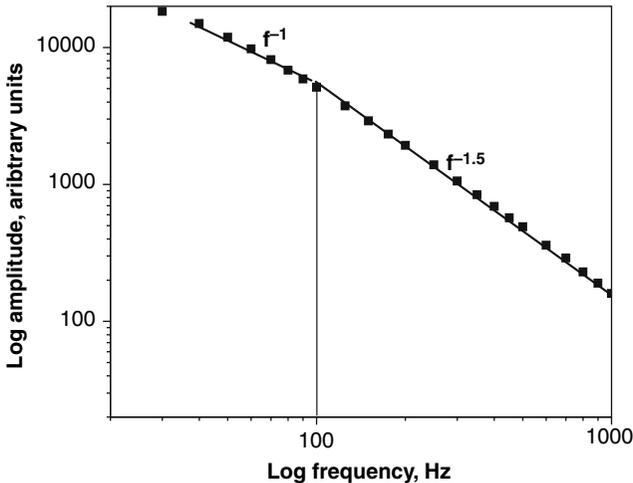


Fig. 3. Log-Log plot of PA amplitude for  $\text{LaPO}_4$  sintered at  $800^\circ\text{C}$ .

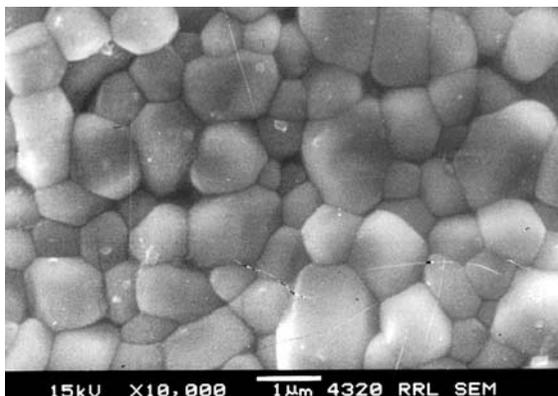


Fig. 4. SEM picture of LaPO<sub>4</sub> ceramics sintered at 1300°C.

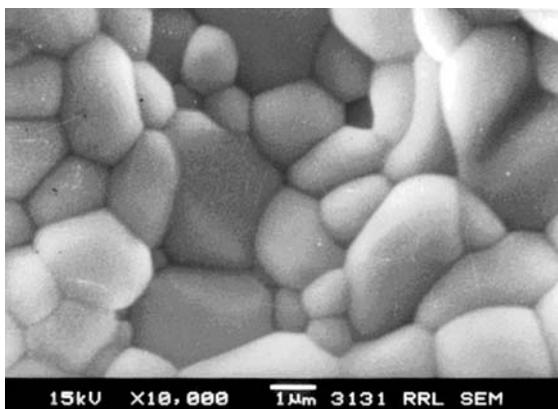
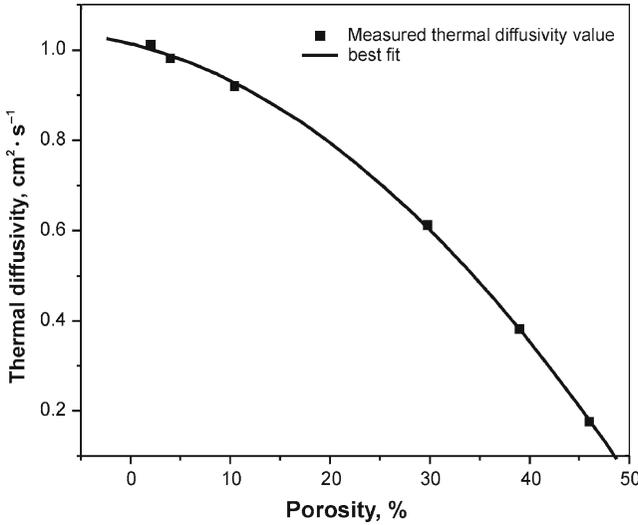


Fig. 5. SEM picture of LaPO<sub>4</sub> ceramics sintered at 1500°C.

phosphate samples, sintered at 1300 and 1500°C are given in Figs. 4 and 5, respectively. The micrograph of the sample sintered at 1300°C shows an average grain size in the range of 1–2  $\mu\text{m}$ . A comparison of micrographs reveals that lanthanum phosphate sintered at 1500°C (Fig. 5) is characterized by larger grains, some of which are slightly deformed. This eventually points to the formation of a liquid phase in samples sintered at temperatures above 1300°C. It should be noted that the formation of a liquid phase at sufficiently high temperatures is generally associated with abnormal grain growth. This could be the reason for the decrease in the density of samples at temperatures above 1300°C.

Thermal properties of ceramics are basically determined by the composition, structure, and arrangements of phases. The appearance of porosity amounts to a new phase in ceramic materials prepared through the gel route. The thermal energy in ceramics is essentially carried away by phonons. The propagation of phonons through the ceramic lattice is greatly influenced by the microstructural features such as pores, grain boundaries, line defects, etc. The influence of porosity on the propagation of phonons, and hence on thermal diffusivity, has been studied in detail [20]. For cases for which the damping wavelength of thermal waves ( $L_{th} = 2\pi\mu$ , where  $\mu = (k_c(p)/(\pi f))^{1/2}$  is the thermal diffusion length of the specimen) is greater than or of the order of the typical grain size ( $L$ ), the ‘thermal disturbance’ is not affected by the heterogeneity of the sample and the measurements then yield the “global thermal diffusivity” [21], which is the case for all the samples in the present study. However, the pores in the lattice act as scattering centers for phonons and hence affect the phonon mean free path and consequently the thermal diffusivity value.

By considering the porous ceramics as a two-phase network in which pores are randomly embedded in a solid matrix, the thermal diffusivity of the specimen is given by the expression,  $k_c(p) = \frac{K_c(p)}{\rho_0 c_0 (1-p)}$ , where  $K_c(p)$  is the thermal conductivity of the specimen having a porosity  $p$ .  $\rho_0$  and  $c_0$  are the density and specific heat capacity, respectively, of the specimen with zero porosity [22]. If the thermal conductivity of the porous material is modified by the same ratio as that of the ratio between the actual density and maximum density, the thermal conductivity is given by the Leob equation [23],  $K_c(p) = K_0(1-p)$ . However, such an approach for the evaluation of the thermal conductivity leads to thermal diffusivity values that are independent of porosity. All the measurements carried out on these ceramic materials reveal that thermal diffusivity values are greatly sensitive to the porosity for samples prepared through the gel route. It has already been reported that the porosity can substantially influence heat transport in SiC ceramics [24]. In order to incorporate the influence of the porosity on the propagation of thermal waves and hence on the thermal diffusivity, Sanchez-Lavega et al. [25] modified the Leob equation as  $k_c(p) = k_0 \frac{(1-\gamma p)}{(1-p)}$ , where  $\gamma$  is an empirical constant. The observed variation in the thermal diffusivity of the specimen under investigation as a function of the porosity (in %) is shown in Fig. 6. From Table I, it is obvious that the measured thermal diffusivity values of all the ceramic samples agree well with the thermal diffusivity values calculated using the modified Leob equation. The variation in porosity with sintering temperature results in a proportional variation in scattering centers for phonons with sintering temperature, consequently resulting in a variation in the phonon mean



**Fig. 6.** Measured thermal diffusivity against porosity of the specimen.

free path. The lattice thermal conductivity (thermal diffusivity), which is also proportional to the phonon mean free path, thus varies in accordance with variations in porosity. The dependence of the porosity on the thermal diffusivity for all the samples under study suggests that the specimens are below the percolation limit.

The calculated value of the empirical constant  $\gamma (= 1.98) > 1$  suggests that the effect of porosity on heat conduction in all the samples under study is not a mere density effect (air holes inside the bulk specimen). More important effects related to porosity and structure of the material may also contribute to a decrease in thermal diffusivity with an increase in porosity [24]. The inverse relation between porosity and thermal diffusivity suggests that the solid area fraction (SAF) in the direction of heat transport essentially determines the thermal diffusivity value [26]. In addition to the pores in the lattice, lattice defects within the grains also affect the propagation of phonons through the lattice. A recent investigation shows that for dense samples, the phonon mean free path is smaller than the grain size at all processing temperatures [27]. Hence, in addition to porosity, the defects in grains also contribute to the variation in thermal diffusivity [28] and this explains the value of  $\gamma > 1$ . Thus, the influence of the sintering temperature and the consequent densification of specimens have great importance in heat transport through ceramics and hence on their thermal diffusivity values.

Apart from the porosity and sintering temperature of ceramic samples, the grain size and thermal contact resistance are two other important factors that affect thermal transport in ceramics. The thermal contact resistance ( $R_T$ ) at the interface is related to the macroscopic thermal conductivity  $K_c$  and to the grain conductivity  $K$  through the relation  $\frac{L}{K_c} = \frac{L}{K} + R_T$ , where  $L$  is the grain size [29]. SEM studies on the ceramic samples sintered at 1300 and 1500°C show that the grain size also varies with the sintering temperature. The variation in thermal diffusivity (thermal conductivity) with porosity results in the variation of the thermal contact resistance and, hence, it influences the heat transport in ceramics. Thus, in addition to porosity, the thermal contact resistance also contributes to variations in the effective thermal diffusivity value.

## 5. CONCLUSIONS

In this article, we have presented measurements of the thermal diffusivity of  $\text{LaPO}_4$  ceramics prepared by the sol-gel route using the laser induced non-destructive photoacoustic technique. The present study shows that the sintering temperature has a great influence on the porosity of ceramics prepared by the gel route. It also confirms that thermal energy transport and propagation of phonons through the ceramic lattice suffer from scattering at the pores of the lattice and results in variations of the thermal diffusivity with porosity. An empirical relation satisfied by the present measurements suggests that the variation in thermal diffusivity with porosity is not merely due to a density effect. The thermal contact resistance is also seen to affect the thermal diffusivity. The present investigation is an example where the measurements carried out by the simple and elegant PA technique can be correlated with the structural variations in the sample. Thus, it is possible to modulate the thermal diffusivity values of ceramic samples by varying the sintering temperature, which has far reaching applications in the microelectronic and optoelectronic industries.

## REFERENCES

1. W. D. Kingery, H. K. Dwen, and D. R. Uhlmann, *Introduction to Ceramics* (Wiley, New York, 1976).
2. Y. Hikichi and T. Nomura, *J. Am. Ceram. Soc.* **70**:C-252 (1987).
3. P. E. D. Morgan and D. B. Marshall, *J. Am. Ceram. Soc.* **78**:1553 (1995).
4. D. M. Liu and W. H. Taun, *Acta Mater.* **44**:813 (1996).
5. J. B. Davis, D. B. Marshall, and P. E. D. Morgan, *J. Eur. Ceram. Soc.* **20**:583 (2000).
6. D. Sh. Tsagareishvili, G. G. Gvelesiani, V. P. Orlovskii, T. V. Belyaevskaya, and V. P. Repko, *Neorg. Mater.* **8**:1790 (1972).

7. W. Min, D. Miyahara, K. Yokoi, T. Yamaguchi, K. Daimon, Y. Hikichi, T. Matsubara, and T. Ota, *Mater. Res. Bull.* **36**:939 (2001).
8. S. D. George, P. Radhakrishnan, V. P. N. Nampoori, and C. P. G. Vallabhan, *Phys. Rev. B* **68**:165319 (2003).
9. S. D. George, P. Radhakrishnan, V. P. N. Nampoori, and C. P. G. Vallabhan, *J. Phys. D: Appl. Phys.* **36**:990 (2003)
10. S. D. George, S. Saravanan, M. R. Anantharaman, S. Venketachalam, P. Radhakrishnan, V. P. N. Nampoori, and C. P. G. Vallabhan *Phys. Rev. B* **69**:235201 (2004)
11. S. D. George, P. Radhakrishnan, V. P. N. Nampoori, and C. P. G. Vallabhan *Appl. Phys. B* **77**:633 (2003).
12. S. D. George, A. A. Anappara, P. R. S. Warriar, K. G. K. Warriar, P. Radhakrishnan, V. P. N. Nampoori, and C. P. G. Vallabhan, *Proc. SPIE* – 5118 (2003), p. 207.
13. M. E. Contreras, J. Serrato, J. Zarate, C. Pacheco, and L. Villasenor *J. Am. Ceram. Soc.* **80**:245 (1997)
14. P. Chen and Tai-il Mah, *J. Mater. Sci.* **32**:3863 (1997).
15. L. Bo, S. Liya, L. Xiaozhen, W. Tianmain, K. Ishii, Y. Sasaki, Y. Kashiwaya, H. Takahashi, and T. Shibayama., *J. Mater. Sci. Lett.* **19**:343 (2000).
16. S. Sankara Raman, V. P. N. Nampoori, C. P. G. Vallabhan, G. Ambadas, and S. Sugunan, *Appl. Phys. Lett.* **67**:2939 (1995) and references therein.
17. A. Calderon, R. A. Munoz Hernaandez, S. A. Tomas, A. Cruz-Orea, and F. Sanchez Sincencio, *J. Appl. Phys.* **84**:6327 (1998).
18. L. F. Perondi and L. C. M. Miranda, *J. Appl. Phys.* **62**:2955 (1987).
19. A. Rosenzweig and A. Gersho, *J. Appl. Phys.* **47**:64 (1976).
20. W. M. Lima, V. Biondo, W. R. Weinand, E. S. Nogueira, A. N. Medina, M. L. Baesso and A. C. Bento, *J. Phys. C: Condens. Matter* **17**:1239 (2005).
21. E. Litoysky, T. Gambaryan-Roisman, M. Shapiro, and A. Shavit, *Trends in Heat, Mass and Momentum Transfer*, Vol. 3 (Council of Scientific Research Integration, Trivandrum, India, 1997), p. 147.
22. J. F. Kerrisk, *J. Appl. Phys.* **42**:267 (1971).
23. H. W. Codbee and W. T. Ziegler, *J. Appl. Phys.* **37**:56 (1966).
24. D. M. Liu, Ch. J. Chen, and L. J. Lin, *J. Appl. Phys.* **75**:3765 (1994).
25. A. Sanchez-Lavega, A. Salazar, A. Ocariz, L. Pottier, E. Gomez, L. M. Villar, and E. Macho, *Appl. Phys. A* **65**:15 (1997) and references therein.
26. M. E. Cunningham and K. L. Peddicord, *Int. Heat Mass Transfer* **24**:1081 (1981).
27. R. W. Rice, *J. Mater. Sci.* **31**:102 (1996).
28. K. Watari, H. Nakano, K. Sato, K. Urabe, K. Ishisaki, S. Cao, and K. Mori, *J. Am. Ceram. Soc.* **86**:1812 (2003)
29. M. V. Swain, L. F. Johnson, R. Syed, and D. P. H. Haseelman *J. Mater. Sci. Lett.* **5**:799 (1988)