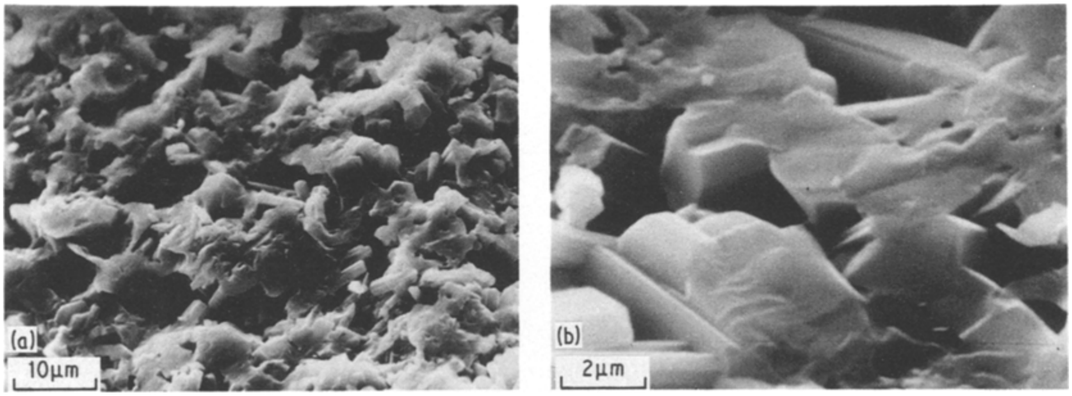

Figure 2 (a and b) Scanning electron micrographs of the fracture surface of a sample pre-treated in H_2 for 1 h and nitrided in N_2.

for the formation of RBSN but rather with the deposition of "massive" CVD-Si_3N_4, as discussed elsewhere [6].

References

1. A. ATKINSON and A. J. MOULSON, *Sci. Ceram.* 8 (1976) 111.
2. W. A. FATE and M. E. MILBERG, *J. Amer. Ceram. Soc.* 61 (1978) 531.
3. D. CAMPOS-LORIZ and F. L. RILEY, *J. Mater. Sci.* 14 (1979) 1007.
4. A. ATKINSON, A. J. MOULSON and E. W. ROBERTS, *J. Amer. Ceram. Soc.* 59 (1976) 285.
5. C. P. GAZZARA and D. R. MESSIER, *Bull. Amer. Ceram. Soc.* 56 (1977) 777.
6. A. J. MOULSON, *J. Mater. Sci.* 14 (1979) 1017.

*Received 19 November
and accepted 12 December 1980*

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X-ray studies on the high pressure behaviour of some rare-earth formates

As part of a programme of high pressure X-ray studies on some solids, the results of the high pressure behaviour of Hg_2Cl_2 [1] and K_2SnCl_6 [2] have previously been reported. Results of a similar study on the formates of lanthanum, cerium and gadolinium [$La(O_2CH)_3$, $Ce(O_2CH)_3$ and $Gd(O_2CH)_3$] rare-earth elements will be presented in this note. These compounds are isomorphous and crystallize in the trigonal system, space group $R3m$, with one molecule per unit cell [3–6]. Recently Hamann [7] studied the infrared (i.r.) spectra of these solids under pressure and reported pressure induced phase transitions. A perusal of the literature shows that no X-ray studies on the high pressure behaviour of these solids seem to be available. In an effort to study the structural changes that occur under pressure, *in situ* X-ray diffraction studies were carried out. This note presents the detailed results of this investigation.

The samples used in the present study were kindly supplied by Dr D. Hamann of CSIRO Applied Chemistry Laboratories, Australia. The details of the growth and purity of these compounds are given by Hamann [7]. The lattice parameters of these compounds determined from the powder patterns on the basis of a rhombohedral lattice with a hexagonal cell are listed in Table I along with the earlier reported values for comparison. The values of the lattice parameters in the present study are slightly higher than the reported ones.

X-ray diffraction data of these compounds at room temperature and at different pressures were obtained using a diamond anvil apparatus

0022–2461/81/082321–03$02.30/0

TABLE I Lattice parameters of lanthanum, cerium and gadolinium formates at room temperature

Compound	Lattice parameter			
	Present study		Earlier study*	
	a (Å)	*c* (Å)	*a* (Å)	*c* (Å)
$La(O_2CH)_3$	10.792 ± 0.002	4.202 ± 0.001	10.74	4.14
$Ce(O_2CH)_3$	10.684 ± 0.002	4.181 ± 0.001	10.67	4.08
$Gd(O_2CH)_3$	10.462 ± 0.002	4.001 ± 0.001	10.44	3.86

*Data taken from ASTM Card Nos 18-674, 14-738 for lanthanum and gadolinium formates, respectively, and from Mayer *et al.* [4] for cerium formate.

(XKB-100) supplied by Materials Research Corporation (USA). To facilitiate the measurements of the diffraction angle, a two film cassette [8] was used to record the diffraction patterns. Two pressure runs were recorded; one with a pressure standard (Ag) and one without a pressure standard. The exposure times ranged from 100 to 200 h. The details of the experimental set-up and the method of estimating the true pressures on the sample have been described in an earlier paper [1].

X-ray diffraction data obtained at ambient pressure and room temperature on the formates of lanthanum, cerium and gadolinium are listed in Table II along with the earlier data for comparison. It can be seen that there is good agreement between the observed and calculated *d*-spacings. At ambient pressure, the reflections 1 1 0, 1 0 1, 0 2 1, 2 2 0, 1 3 1 and 1 0 2 could be recorded very clearly. As the pressure was increased the intensity of the reflections 1 0 1 and 1 0 2 gradually decreased in all the materials. In the patterns obtained at a pressure of about 40 kbar, the reflection 1 0 1 completely disappeared. At ambient pressure the reflections 1 0 1, 0 2 1 and 2 2 0 have an almost equal intensity. The disappearance of the equally intense 1 0 1 reflection and the appearance of two other reflections, 0 2 1 and 2 2 0, (indexed as 2 2 0 and 2 2 2 in the new phase) at about 40 kbar and room temperature may be due to a phase change of these solids. This has been observed by Hamann [7] in his infrared spectral studies of these compounds. Unfortunately little is known about the solid-state phase transitions of these solids. The infrared spectra under pressure [7] alone is not sufficient to assign the high pressure phase of these solids. On the other hand, the limited number of reflections in the new phase of these solids in the present investigation hampers the conventional structural analysis. However, the disappearance of some reflections under pressure may be connected with a change in symmetry of these solids to a higher co-ordination. Based on this assumption, the patterns recorded at about 40 kbar could be indexed on the basis of a cubic lattice with lattice constants $a = 7.46$, 7.42 and 7.18 Å for lanthanum, cerium and gadolinium formates, respectively. The observed *d*-spacings and intensities along with the calculated values for these solids at about 40 kbar are listed in Table III. Good agreement was found between the observed and calculated *d*-spacings. An examination of the observed reflections show a body-centred cubic unit cell for these compounds. However, because of the limited number of reflections in the high pressure phase of these solids, it was not possible

TABLE II X-ray diffraction data for the rhombohedral lattice phase with a hexagonal cell for lanthanum, cerium and gadolinium formates at atmospheric pressure and ambient temperature

$La(O_2CH)_3$				$Ce(O_2CH)_3$				$Gd(O_2CH)_3$			
d_{obs} (Å)	d_{cal} (Å)*	*h k l**	I_{obs}†	d_{obs} (Å)	d_{cal} (Å)‡	*h k l*‡	I_{obs}†	d_{obs} (Å)	d_{cal} (Å)*	*h k l**	I_{obs}†
5.46	5.41	1 1 0	s	5.41	5.34	1 1 0	s	5.20	5.22	1 1 0	s
3.82	3.79	1 0 1	m	3.77	3.73	1 0 1	m	3.60	3.64	1 0 1	m
3.10	3.09	0 2 1	m	3.09	3.06	0 2 1	m	2.93	2.99	0 2 1	m
2.70	2.68	2 2 0	ms	2.68	2.67	2 2 0	ms	2.56	2.61	2 2 0	ms
2.16	2.19	1 3 1	w	2.18	2.17	1 3 1	w	2.10	2.13	1 3 1	w
2.01	2.02	4 1 0	w	2.01	2.02	4 1 0	w	1.95	1.98	4 1 0	w
1.89	1.89	3 2 1	mw	1.88	1.88	3 2 1	mw	1.83	1.84	3 2 1	mw

*Data taken from ASTM Card Nos 18-674, 14-738 for lanthanum and gadolinium formates, respectively.

†I_{obs} are visual estimated intensities (s–strong, ms–medium strong, m–medium, w–weak, and mw–medium weak).

‡Data taken from Mayer *et al.* [4].

TABLE III X-ray diffraction data for the cubic phase of lanthanum, cerium and gadolinium formates at 40 kbar and ambient temperature*

$La(O_2CH)_3$				$Ce(O_2CH)_3$				$Gd(O_2CH)_3$			
d_{obs} (Å)	d_{cal} (Å)	*hkl*	I_{obs}†	d_{obs} (Å)	d_{cal} (Å)	*hkl*	I_{obs}†	d_{obs} (Å)	d_{cal} (Å)	*hkl*	I_{obs}†
5.30	5.28	110	s	5.28	5.25	110	s	5.10	5.08	110	s
3.06	3.05	211	m	3.03	3.03	211	m	2.92	2.93	211	m
2.64	2.64	220	ms	2.64	2.62	220	ms	2.54	2.54	220	ms
2.13	2.15	222	w	2.13	2.14	222	w	2.05	2.07	222	w
1.99	1.99	321	mw	1.98	1.98	321	mw	1.93	1.92	321	mw

*Indexing is made assuming a cubic lattice with lattice parameter a = 7.46, 7.42 and 7.18 Å for lanthanum, cerium and gadolinium formates, respectively. d_{cal} are the d-spacings calculated from these parameters.

†I_{obs} are visual estimated intensities (s–strong, ms–medium strong, m–medium, w–weak and mw–medium weak).

to confirm the space group unambiguously. Although there is a slight discontinuity in the unit cell volume of these solids at the transition point, it could not be decided unambiguously that the transition is second order. The reasons for this are that the transition is very sluggish and as such the change in the unit cell dimensions below the transition could not be studied. Further, the lattice parameters of the new phase were calculated from a diffraction pattern which was recorded at a slightly higher pressure than the transition pressure. Our present X-ray data on the high pressure behaviour of these solids do not allow a detailed structural analysis. More information on the changes in various physical properties at the transition point and a detailed analysis at the high pressure phase would be needed to allow more detailed discussion of the high pressure phase of these compounds.

Acknowledgement

The authors acknowledge with sincere thanks Dr D. Hamann, for providing them with the samples used in the present investigation and for many useful suggestions. One of the authors (P. Kistaiah) is grateful to the CSIR, New Delhi, India, for the award of a Research Fellowship.

References

1. T. RANGA PRASAD, K. SATHYANARAYANA MURTHY, LEELA IYENGAR and K. V. KRISHNA RAO, *Pramana* **12** (1979) 523.
2. P. KISTAIAH, K. SATHYANARAYANA MURTHY, LEELA IYENGAR and K. V. KRISHNA RAO, *ibid.* **15** (1980) 475.
3. A. PABST, *J. Chem. Phys.* **11** (1943) 145.
4. I. MAYER, M. STEINBERG, F. FEIGENBLATT and A. GLASNER, *J. Phys. Chem.* **66** (1962) 1737.
5. V. E. PLYUSHCHEV, L. P. SHKLOVER and L. M. SHKOL'NIKOVA, *J. Struct. Chem.* **5** (1964) 733.
6. *Idem, ibid.* 7 (1966) 687.
7. S. D. HAMANN, *High Temp. – High Press.* **9** (1977) 57.
8. A. K. SINGH, *Rev. Sci. Instrum.* **43** (1972) 1311.

Received 25 November
and accepted 12 December 1980

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