JOURNAL OF MATERIALS SCIENCE 29 (1994) 6335–6339

Fluorination of $REBa_2VO_6$ compounds

G. ABDULKARIM, U. R. K. RAO*‡, G. B. KALE, RAM PRASAD
Metallurgy Division, and ‡ Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

R. NAGARAJAN
Tata Institute of Fundamental Research, Bombay 400 005, India

New compounds of the type $REBa_2VO_4F_4$ where RE = Y, Eu and Sm have been prepared for the first time by reacting $REBa_2VO_6$ with NH_4HF_2 used as a low-temperature fluorinating agent. Thermogravimetric analysis/differential thermal analysis, chemical analysis, ^{151}Eu Mössbauer and EPMA evidence for the formation of the fluorinated compound is presented.

1. Introduction

Ammonium bifluoride has been used in a number of instances as a fluorinating agent at room temperature to prepare fluoro- and oxyfluoro-anionic compounds [1–4]. More recently it has found application [5–7] in introducing fluorine in place of oxygen in the 1, 2, 3 superconducting oxide $YBa_2Cu_3O_{6.5+\delta}$. By using a similar procedure, some of the compounds of the type $REBa_2VO_6$ (where RE = yttrium, europium and samarium), have been fluorinated to give $REBa_2VO_4F_4$ as described in this paper.

2. Experimental procedure

The materials employed in this study were $REBa_2VO_6$, prepared as described earlier [8–10], and NH_4HF_2 of BDH LR quality. The reaction was conducted by intimately grinding together the constituents, followed by heating. The thermogravimetric/differential thermal analysis (TG/DTA) equipment used was an Ulvac Sinku Riko TGD model 7000 RHP with a heating/cooling rate of 10 °C min^{-1} in static air with sample size of around 30 mg. The XRD powder patterns were run using nickel-filtered CuK_α radiation.

Determination of the metal content in the compounds $EuBa_2VO_6$ and $EuBa_2VO_4F_4$ was undertaken by chemical analysis and by electron microprobe analysis (EPMA). In order to determine by chemical analysis the europium, barium and vanadium content in the compound $EuBa_2VO_6$, the following procedure was employed. A known weight of the sample was fumed with perchloric acid to dryness; the residue was dissolved in H_2O and diluted to a known volume. This was used as the stock solution. Barium in the solution was estimated by precipitating it as $BaSO_4$. The filtrate was used to determine the vanadium content as $(VO)_2$ $(OH)_3$ by the colorimetric method after oxidizing with H_2O_2. The europium content in the solution was determined gravimetrically as Eu_2O_3. The fluorine content was determined by Krishnamoorthy *et al.* [11] using a fluoride-ion selective electrode.

A Camebal EPMA apparatus was used to determine the homogeneity in elemental composition of the compounds $EuBa_2VO_6$ and $EuBa_2VO_4F_4$. The accelerating voltage was 15 keV with a beam current of 100 nA. BaF_2, vanadium metal and Eu_2O_3 were used as standards for barium, fluorine, vanadium and europium. An LiF crystal was used to diffract BaL_α and EuL_α lines. A TAP crystal was used for FK_α lines. ZAF corrections are applied by the built in software of the instrument.

3. Results and discussion

Two mechanical mixtures of $REBa_2VO_6$ and NH_4HF_2 in the ratios 1:6 and 1:8 were prepared by mixing the compounds in polythene bags. The XRD patterns of the mechanical mixtures taken immediately after mixing showed that the reaction had partially taken place. The mixture was heated in a platinum crucible at different temperatures in the range 300–700 °C for different times and progress of the reaction was monitored by powder X-ray diffraction (XRD). In both the mixtures containing YBa_2VO_6, a new compound was obtained (Fig. 1) on heating at 600 for 2 h. The same product was obtained on heating even the 1:16 mixture. In the case of the europium sample, a new compound was obtained when either the 1:6 or the 1:8 mixture was heated at 550 °C for 2 h. In other cases where RE = samarium, holmium and europium, fluorination was tried by taking $REBa_2VO_6$ and NH_4HF_2 in the ratio 1:8. It was observed that the fluorinated compound was formed in the case of samarium when heated at 450 °C for 2 h. In the cases of holmium and erbium, the product at 450 °C was a mixture of BaF_2, RE_2O_3 and $Ba_3(VO_4)_2$. The powder XRD patterns of all the fluorinated products, wherever formed, were indexed on the basis of a cubic unit cell (Tables I–III). Table IV gives the results of fluorine analysis on heat-treated

---

* Author to whom all correspondence should be addressed.

0022–2461

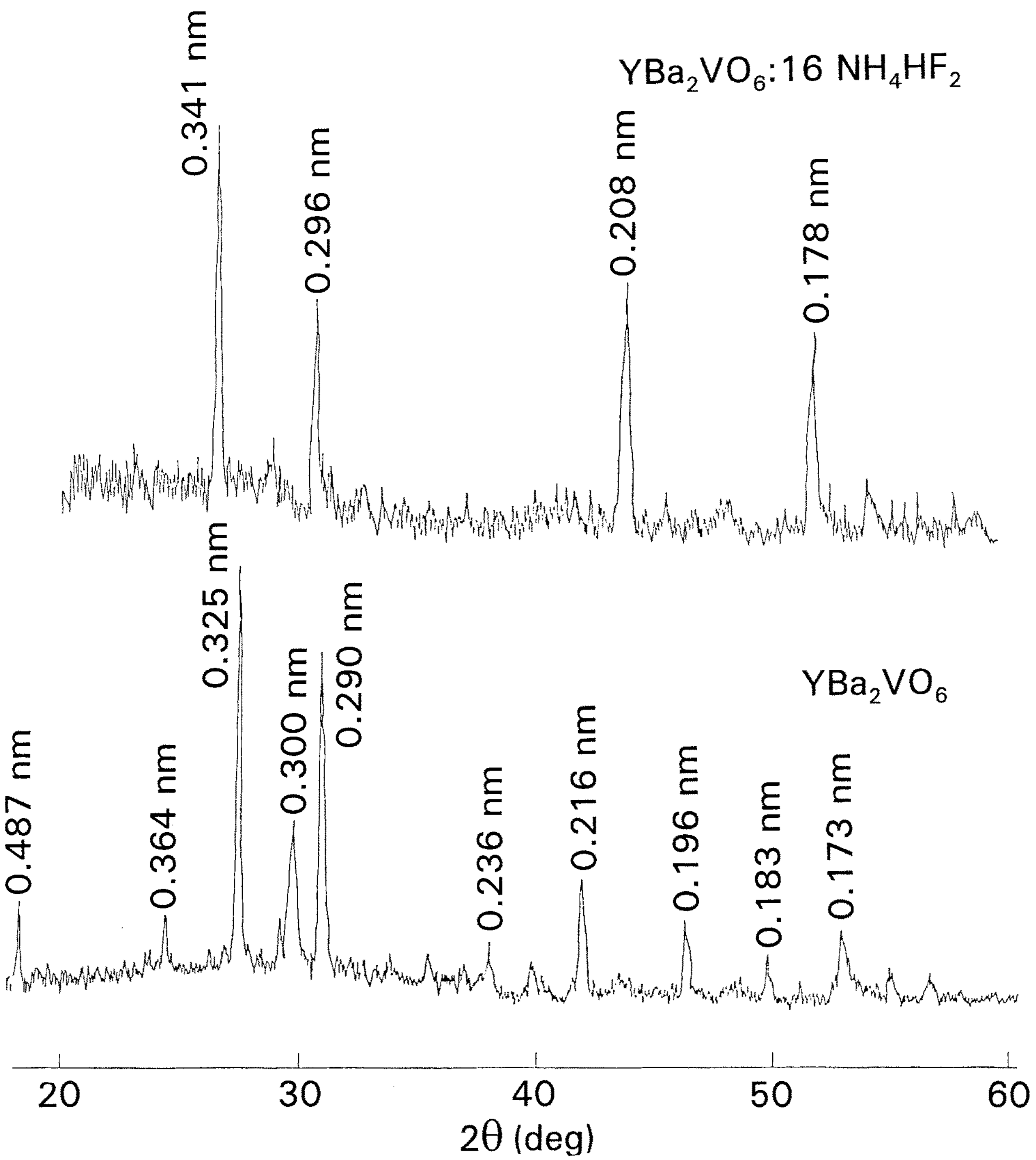

Figure 1 Powder XRD pattern of YBa_2VO_6 and of the mixture YBa_2VO_6: $8NH_4HF_2$ after heating at 600 °C for 2 h.

TABLE I Fit of the powder XRD pattern of $YBa_2VO_4F_4$. Cubic, $a = 0.591 \pm 0.0003$ nm

d_{obs} (nm)	d_{cal} (nm)	Int	*hkl*
0.3410	0.3412	100	111
0.2960	0.2955	30	200
0.2089	0.2089	60	220
0.1782	0.1782	50	113

mixtures. The observed fluorine content agrees with that expected for the fluorinated product having the general formula $REBa_2VO_4F_4$. The following path is proposed for the reaction.

$$REBa_2VO_6 + nNH_4HF_2 \rightarrow REBa_2VO_4F_4 + nNH_3 + 2(n-2)HF + 2H_2O \quad (1)$$

All the above fluorinated compounds decompose at higher temperatures in the following manner, as corroborated by powder XRD

$$3REBa_2VO_4F_4 \rightarrow Ba_5F(VO_4)_3 + 3REF_3 + BaF_2 \quad (2)$$

The course of this decomposition was further confirmed by determining the fluorine content of the mixture in the product as given in Table V. The data on the TG runs on the mechanical mixtures (Fig. 2), summarized in Table VI, are in agreement with those expected, based on Reaction 1 and with those obtained from the chemical analysis. The weight loss levels off beyond

TABLE II Fit of the powder XRD pattern of $EuBa_2VO_4F_4$. Cubic, $a = 0.5968 \pm 0.0002$ nm

d_{obs} (nm)	d_{cal} (nm)	Int	*hkl*
0.3430	0.3446	100	111
0.2970	0.2984	45	200
0.2109	0.2110	59	220
0.1800	0.1800	47	311

TABLE III Fit of the XRD pattern of $SmBa_2VO_4F_4$. Cubic, $a_0 = 0.6131 \pm 0.0005$ nm

d_{obs} (nm)	d_{cal} (nm)	Int	*hkl*
0.3540	0.3540	100	111
0.3118	0.3066	70	200
0.2182	0.2168	52	220
0.1863	0.1850	40	311

TABLE IV Fluorine content by chemical analysis in the heat-treated mixture

Starting mixture	Amount of F observed in product[a] (wt %)	Amount of F expected for $REBa_2VO_4F_4$ (wt %)
$YBa_2VO_6:6NH_4HF_2$	14.1	13.7
$YBa_2VO_6:8NH_4HF_2$	14.4	13.7
$YBa_2VO_6:16NH_4HF_2$	14.5	13.7
$EuBa_2VO_6:6NH_4HF_2$	12.8	12.3
$EuBa_2VO_6:8NH_4HF_2$	13.0	12.3
$SmBa_2VO_6:8NH_4HF_2$	10.0	10.6

[a] Estimated error is ± 1%.

TABLE V Chemical analysis of decomposed $REBa_2VO_4F_4$

Starting compound	Amount of F observed (wt %)[a]	Amount of F calculated from Reaction 2 (wt %)
$YBa_2VO_4F_4$	14.1	13.7
$EuBa_2VO_4F_4$	12.5	12.3

[a] Estimated error is ± 1%.

TABLE VI Summary of TG data

Composition of mixture	Loss calculated from Reaction 1 (wt %)	Loss observed in TG (wt %)
$YBa_2VO_6:6NH_4HF_2$	35	34
$YBa_2VO_6:8NH_4HF_2$	42	37
$YBa_2VO_6:16NH_4HF_2$	61	63
$EuBa_2VO_6:6NH_4HF_2$	33	33
$EuBa_2VO_6:8NH_4HF_2$	41	40
$SmBa_2VO_6:8NH_4HF_2$	41	39

400 °C, showing that all the volatile products, such as HF, NH_3 and H_2O, are driven off. The DTA runs (Fig. 3) show four endotherms at 70, 110, 150 and 210 °C. The first weak endotherm is attributed to loss of

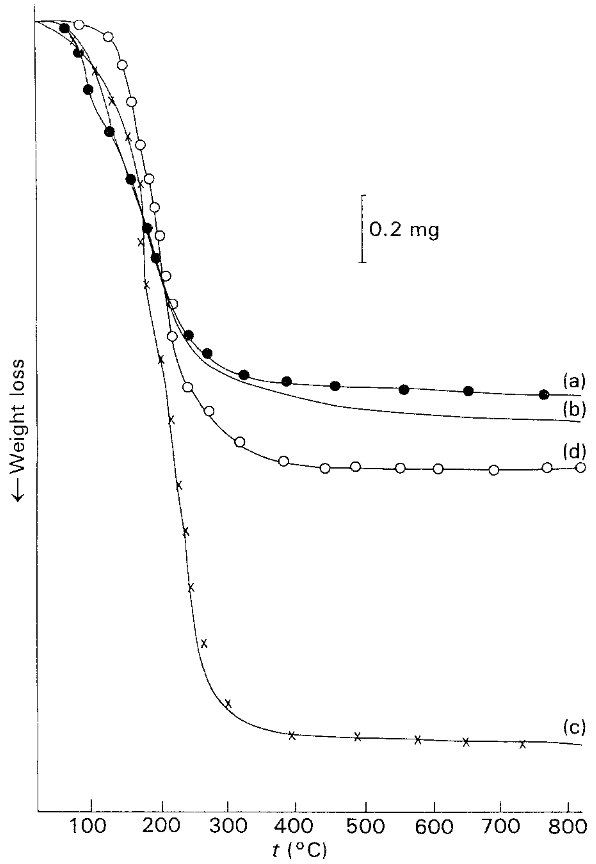

Figure 2 TGA patterns of NH_4HF_2 and a mechanical mixture of NH_4HF_2 with YBa_2VO_6. Sample size: (a) 30.5 mg, (b) 31.6 mg, (c) 32.7 mg and (d) 31.9 mg. (a) $YBa_2VO_6:6NH_4HF_2$, (b) $YBa_2VO_6:8NH_4HF_2$, (c) $YBa_2VO_6:16NH_4HF_2$, (d) NH_4HF_2.

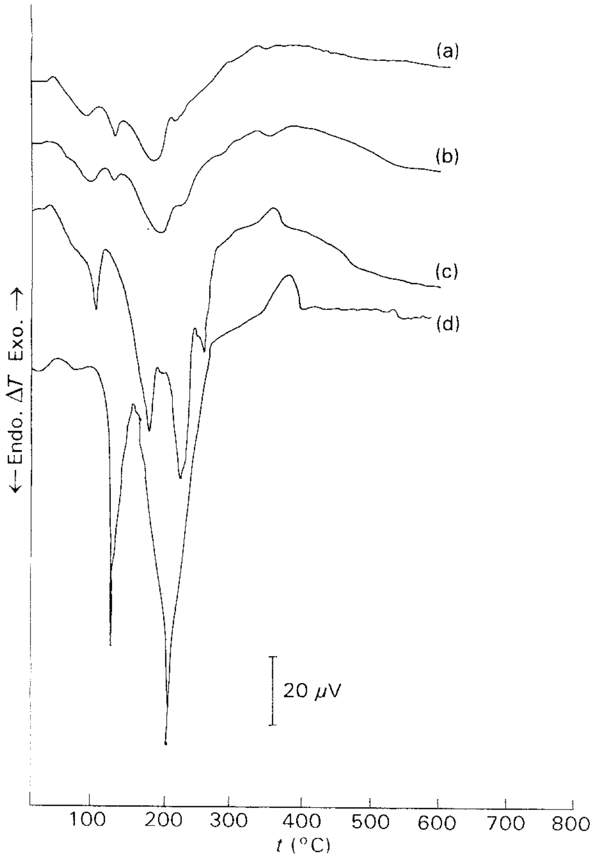

Figure 3 DTA run of NH_4HF_2 and of mechanical mixtures of NH_4HF_2 with YBa_2VO_6. Sample sizes and compounds as in Fig. 2.

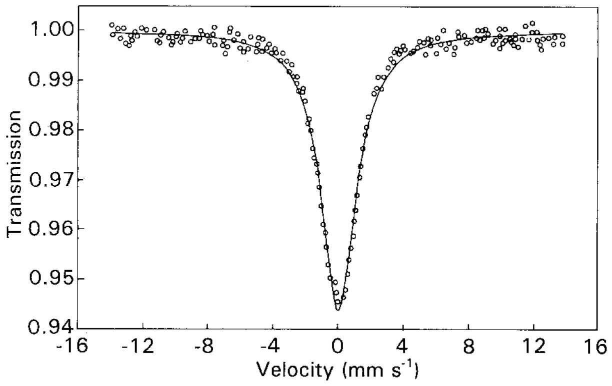

Figure 4 ^{151}Eu Mössbauer spectrum of $EuBa_2VO_4F_4$ at room temperature. The reference is EuF_3.

occluded moisture. The other endotherms may be attributed to melting and decomposition of unreacted NH_4HF_2 to form NH_3 and HF. The XRD evidence, chemical analysis and TG/DTA data provide circumstantial evidence for the presence of fluorine in the product, but a doubt persists whether or not fluorine forms part of the lattice in the product. Therefore, the ^{151}Eu Mössbauer spectrum of the fluorinated $EuBa_2VO_4F_4$ (Fig. 4) was recorded. The chemical state of the europium in the fluorinated compound can be distinctly determined from its isomeric shift (IS) in its ^{151}Eu Mössbauer spectrum. The shifts of the divalent and trivalent europium compounds are widely different. The Eu^{3+} compounds show IS in the range 0–0.1 mm s^{-1} and Eu^{2+} compounds in the range -10 to -14 mm s^{-1} with respect to EuF_3. ^{151}Eu Mössbauer resonance for the reaction product of the $EuBa_2VO_6$:$8NH_4HF_2$ mixture was recorded at room temperature. The spectrum showed a single narrow line with an IS of 0.153 ± 0.05 mm s^{-1}. This is different from that of the parent compound, $EuBa_2VO_6$, IS = 0.53 ± 0.05 mm s^{-1} or from that of all the possible products of the reaction, EuF_3 (0.00 mm s^{-1}) and Eu_2O_3 (1.05 ± 0.05 mm s^{-1}). Europium in the fluorinated product is present in its + 3 valence state. The Mössbauer result in conjunction with XRD data is taken as evidence for the incorporation of fluorine in the lattice.

The results of chemical analysis are given in Table VII, and those for EPMA on $EuBa_2VO_6$ and $EuBa_2VO_4F_4$ are given in Tables VIII and IX. The results are consistent in the case of the compound $REBa_2VO_4$. But in the fluorinated compound, the fluorine content is found to be more than that obtained from chemical analysis and the vanadium content is found to be slightly lower than expected. They are probably inherent in the standards used.

It was found [7] that $YBa_2Cu_3O_{6.5+\delta}$ could be fluorinated to a maximum extent with the composition $YBa_2Cu_3O_3F_7$ whereas, in the present case of $REBa_2VO_6$, the highest fluorinated product has the composition $REBa_2VO_4F_4$. The lattices of the product appear to decide the maximum amount of fluorine that can replace oxygen atoms in the compounds.

On the basis of the above results, it is concluded that (a) it is possible to fluorinate the compounds $REBa_2VO_6$ where RE = yttrium, europium and samarium using NH_4HF_2, (b) chemical analysis, thermal analysis, EPMA and Mössbauer studies (in case of the europium compound) carried out on these fluorinated compounds are consistent with the general formula $REBa_2VO_4F_4$ for the product, and (c) fluorination was not possible in the compounds of holmium and europium probably due to the instability of the fluorinated compounds at the temperature of synthesis.

TABLE VII Chemical analysis of $EuBa_2VO_6$

Element	Observed content (wt %)	Calculated content (wt %)
Europium	26.4	26.6
Barium	47.4	47.8
Vanadium	9.0	8.9

TABLE VIII EPMA analysis of $EuBa_2VO_6$

Element	Observed content (wt %)	Calculated content (wt %)
Europium	26.5	26.5
Barium	48.5	47.8
Vanadium	8.4	8.9
Oxygen	16.5	16.7

TABLE IX EPMA of $EuBa_2VO_4F_4$

Element	Observed content (wt %)	Calculated content (wt %)
Europium	22.3	24.6
Barium	43.4	44.4
Vanadium	6.8	8.2
Fluorine	17.6[a]	12.3
Oxygen	9.8	10.3

[a] The difference probably arises out of the choice of reference of BaF_2, for barium in the EPMA.

Acknowledgements

The authors thank Dr Satyabrat for the TG/DTA support, and Dr P. N. Moorthy, Head, Applied Chemistry Division and Dr S. Banerjee, Head, Metallurgy Division, Bhabha Atomic Research Centre, for their interest in the work.

References

1. J. SANIAVILLIE, in "Proceedings of the 2nd United Nations International Conference on Peaceful Uses of Atomic Energy", Geneva, Vol. 4 (1958) p. 103.
2. B. R. WANI, U. R. K. RAO, K. S. VENKATESWARLU and A. S. GOKHALE, *Thermochim. Acta* **58** (1982) 87.
3. B. N. WANI and U. R. K. RAO, *Synth. React. Inorg. Metal-organ. Chem.* **21** (1991) 779.
4. S. V. ADHYAPAK, B. N. WANI, U. R. K. RAO and S. K. KULSHRESHTHA, *ibid.* **22** (1992) 337.
5. U. R. K. RAO, A. K. TYAGI, S. J. PATWE, R. M. IYER, M. D. SASTRY, R. H. KADAM, Y. BABU and A. G. I. DALVI, *Solid State Commun.* **67** (1988) 385.

6. U. R. K. RAO, A. K. TYAGI, S. J. PATWE and R. M. IYER, *Pramana J. Phys.* **31** (1988) L 79.
7. A. K. TYAGI, U. R. K. RAO, R. M. IYER, A. K. RAJARAJAN and L. C. GUPTA, *J. Mater. Sci. Lett.* **11** (1992) 1288.
8. G. ABDUL KARIM, U. R. K. RAO and RAM PRASAD, *ibid.* **7** (1988) 300.
9. *Idem, ibid.* **7** (1988) 1239.
10. G. ABDUL KARIM, U. R. K. RAO, RAM PRASAD and R. NAGARAJAN, *ibid.* **11** (1992) 828.
11. T. S. KRISHNAMOORTHY, N. MAHADEVAN, S. S. DESAI and C. C. DIAS, *Pramana J. Phys.* **32** (1989) 143.

Received 10 March 1993
and accepted 5 May 1994