INTRODUCTION

The compounds of 3d transition elements have been extensively studied and many useful materials both form theoretical and application point of view have been obtained. Trivalent zirconates have been an exception in this regard. The first attempt to form such compounds was done by Nassau. Besides this, very little data are available on these compounds. This lack of study prompted us to prepare and investigate magnetic and electrical properties of these compounds. The electrical transport properties of iron and cobalt zirconates are reported in this paper.

EXPERIMENTAL

Material and Methods

The starting materials for the preparation of iron and cobalt zirconates were their respective sesquioxides Fe$_2$O$_3$ and Co$_2$O$_3$ (procured from Rare and Research Chemicals, India, with stated purity of 99.99%) and ZrO$_2$ (from Bonds India, with stated purity of 99.99%). All these oxides were dried around 500 K before use. The stoichiometric amount of starting materials were thoroughly mixed, made into pellets and fired around 700K in a platinum crucible in air for 24h. The reaction product after grinding, again made into pellets and fired around 800K for more than 24h. This process has been found sufficient for the formation of single phase compound as evident from X-ray diffraction (XRD) pattern and their analysis.

RESULTS AND DISCUSSION

Electrodes play an important role in the measurement of s and S. The stringent criteria is to have ohmic contact in both the measurements. We have used platinum foil (thickness ~ 0.02 mm), pressed mechanically on the pellet faces as electrodes. The ohmic contact was confirmed by linear current density (J) against applied d.c. electric field plot at constant temperature. The current density has also been measured as a function of
time keeping temperature and applied d.c. electric field constant. J values have been found almost independent of time indicating that electrical current in these solids is completely electronic.

The air pores and grain boundaries, which have a significant effect on the values of s and S, cannot be avoid in pellets but can be significantly reduced in highly pressed pellets of uniform density. The pellets used in our measurements were made using fine and uniform grain powders at pressures exceeding $8 \times 10^8 \text{ N m}^{-2}$ and sintered around 800 K for two days in air. It has been observed that pellets of different dimensions yield almost the same values of s and S. Further s has also been found independent of a.c. frequency (0 to $10^5 \text{Hz}$). The independence of s from dimensions, palletizing pressure and signal frequency indicates that measured values of s represent the bulk value of the material and grain boundary effects are considerably reduced. The s values have been further corrected for air pores using relations $9$.

The $\sigma$ and S measurements on few pellets of each material have been carried out in air in a temperature range of 500-1200K. The value of s and S and their variation with temperature do not differ considerably from sample to sample. The average of s and S on few pellets have been taken as their representative value. The log s and S against inverse of temperature plots for studied materials show linear regions in some temperature intervals and can be represented by the relations.

$$\sigma = \sigma_0 \exp \left(-\frac{E_a}{kT}\right) \quad \text{(1)}$$

$$S = \eta/\rho T + H \quad \text{(2)}$$

where $\sigma_0$, $E_a$, $\eta$, and H are constants. The evaluated values of these constants for studied materials in linear regions are given in Table. The nature of the majority charge carrier has been obtained on the basis of the sign of S and is also given in Table.

From the study of time dependence of d.c. electrical conductivity, it has been concluded that studied zirconates are essentially electronic conductors. Electrical conduction in them can be explained using simple energy band model. The relevant electron energy bands which may be important in these solids are $\text{O}^{2-} : 2p$, $\text{M}^{3+} : 3d$, $\text{M}^{3+} : 4s$ and $\text{Zr}^{4+} : 4d$ in order of increasing energy. The last two bands are empty and $\text{M}^{3+} : 3d$ bands is partially filled. Thus according to band theory these zirconates should be metallic. But it is not so, they are almost insulators. It can, therefore, be concluded that $\text{M}^{3+} : 3d$ band is narrow and unable to support metallic conduction. Hence 3d electrons either do not take part in electrical conduction or if they do so, it is through a low mobility small polaron (localized electrons in 3d bands behave as a small polaron). On the basis of above discussion one can draw a schematic energy band diagram. This energy band diagram can be used to explain the genesis of charges carriers and conduction process in these solids.

Looking at the summarized results of s and S given in Table, the intrinsic energy band conduction seems to be the suitable mechanism. The relevant bands which take part into conduction process are $\text{O}^{2-} : 2p$ as valence band and $\text{M}^{3+} : 4s$ as conduction band.

| Material  | $\sigma$ measurement | S measurement |
|-----------|----------------------|---------------|
|           | Temp range (K) | $E_a$ (eV) | $\sigma_0$ | $s_0$ (\(\Omega^{-1} \text{ m}^{-1}\)) | Temp range (K) | $\eta$ (eV) | H (\(-\text{mV} \text{K}^{-1}\)) | $T_\eta$ (K) | Charge carrier |
| FeZrO$_5$ | 500-710 | 1.07 | 4.13×10$^2$ | 200 - 680 | -0.12 | + 0.07 | 7800 | h |
|           | 810-1200 | 1.28 | 3.05×10$^4$ | 810 - 1200 | -0.02 | - 0.03 | - | h |
| CoZrO$_5$ | 500-695 | 1.05 | 1.60×10$^2$ | 500 - 625 | -0.10 | + 0.08 | 760 | h |
|           | 810-1200 | 1.28 | 6.23×10$^3$ | 850-1200 | -0.02 | - 0.03 | - | h |

Table 1: Summarized results of $\sigma$ and S measurements
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