Studies on Structural and Dielectric Properties of Defect Pyrochlore-type ABMoO$_6$ Ceramics

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Abstract

Polycrystalline samples of the defect pyrochlore-type ABMoO$_6$ (A = Li, Na, K, Tl, Cs; B = Nb, Ta) compounds were prepared by solid-state reaction technique. The formation of the compounds was checked by x-ray diffraction technique. All the compounds were found to have cubic crystal structure at room temperature. Dielectric parameters (ε, tanδ) were measured as a function of frequency (10^3 -10^6 Hz) and temperature (100 – 500 K). Some compounds have dielectric anomaly in the above temperature range.

Keywords: Ceramics, Defect Pyrochlore, Dielectric property

1. Introduction

Ceramic materials find applications in fuel cells, solid-state batteries and gas sensors because of their high ionic conductivities. The physical rigidity and inertness of ceramic makes it useful where a liquid electrolyte would be impractical. There are different types of skeleton structures which facilitate fast ion conduction. Among all the three-dimensional skeleton structures, pyrochlores offer interesting possibilities to act as fast ion conductors. The cubic pyrochlores have a general formula A$_2$B$_2$X$_6$Y where A is large cation, B is a small cation octahedrally coordinated by six X ions and Y is O, OH, F, H$_2$O. The B$_2$X$_6$ sub-array forms a rigid skeleton of corner – shared octahedra [1]. These octahedral are arranged in a tetrahedral array according to a diamond-type net and a system of open channel is observed. It is the presence of these channels which makes pyrochlores potentially useful. In normal pyrochlores, the channels contain an array of stoichiometry (A$_2$Y)$_n$ unit. The chemical bond between the rigid framework and the array may be more or less weak according to the chemical composition, but is critical in determining the chemical and physical properties. In fact, because of the weakness of that interaction, atoms A and Y may be partly or completely missing giving rise to 'defect' pyrochlores. 'Defect' pyrochlores have a B$_2$X$_6$ network similar to regular pyrochlores but with vacancies introduced in the A$_2$Y array. Thus these compounds are generally formulated as □AB$_2$X$_6$□ or □$_2$B$_2$X$_6$A (□: vacancy) depending on the size of A cation. These are the most interesting ones making fast ion conduction possible for having structural disorder. These types of compounds have a tendency of getting contaminated by absorbing moisture from surroundings. Compounds with larger lattice parameter become hydrates on exposure to air. Defect pyrochlores with small A$^+$ ion (i.e., Li$^+$, Na$^+$, etc.) are all hydrated at room temperature. Reasonably dense specimens (having 99% of theoretical density) also absorb water from atmosphere. The absorbed water can be removed by heating the specimens. Here structural and dielectric properties of some members of defect pyrochlore family having general formula ABMoO$_6$ (A = Li, Na, K, Tl, Cs; B = Nb, Ta) are reported [2-7].

2.   Materials and Methods

The proposed compounds were prepared from the pure carbonates and oxides: Li_2CO_3 (99%, M/s Loba Chemie Indoaustranal Co., India), Na_2CO_3 (99%, M/s Sarabhai Chemicals, India), K_2CO_3 (99%, M/s Sarabhai Chemicals, India), Tl_2CO_3 (99%, Jhonson Matthey Chemicals Ltd., England), Cs_2CO_3 (99%, Lancaster, England), Nb_2O_5 (99%, BARC, India), Ta_2O_5 (99%, M/s E. Merck, Germany) and MoO_3 (99%, M/s Loba Chemie Pvt. Ltd.,India). Conventional high-temperature solid-state reaction technique was used to synthesise the compounds. The stoichiometrically weighed constituents for a particular composition were thoroughly mixed in agate mortar for 2 hours. The mixed powders were then calcined in alumina crucible at 773 K for 15 hours in air. The initially calcined powders were ground once again and recalcined at some higher temperatures in the same atmosphere. This practice was repeated several times till the formation of the compounds. The completion of reaction was checked by X-ray diffraction technique (XRD). The XRD pattern of calcined powder was obtained by using X-ray powder diffractometer (Rigaku Miniflex, Japan) with CuK_α radiation ($\lambda = 1.5418$ Å) in the Bragg angle range 20° - 70° at a scanning rate of 2° min^{-1}. The fine homogeneous recalcined powders were cold pressed into cylindrical pellets (discs) at a pressure $\sim 5 \times 10^6$ Pa. An organic solution (Polyvinyl Alcohol – PVA) was used as binder to reduce the brittleness of the pellets. These pellets were sintered for 6 hours in air. The organic binder was burnt out during high temperature sintering. The diameter of the green samples was reduced by 0.5% after sintering. The thickness of the pellets was 1-3 mm. The samples were cooled down to room temperature by rapid cooling process. The final calcination temperature and time, sintering temperature and time have been given in   Table 1. The sintered pellets were polished with fine emery paper to make both the surfaces flat and parallel. The pellets were electroded with high purity silver paste for electrical measurements. Some researchers [8, 9] had reported that the electrode material did not affect the dielectric and electrical properties of the compounds. The dielectric parameters (ε, $\tan\delta$) were measured as a function of frequency (10^3 -10^6 Hz) and temperature ($100 – 500$ K) using GR1620AP capacitance measuring assembly and HP 4342A Q-meter along with laboratory-made three-terminal sample holder and heating arrangements. As most of the members of the defect pyrochlore family have a tendency to get contaminated by moisture, special care was taken to avoid the problem. All the samples were kept at 400K for 12 h before each experiment. In order to prevent rehydration of the samples during experiments silica gel was kept inside the sample holder. The structural data presented here are of hydrated (i.e., room temperature) phase of the compounds whereas the dielectric data are of their anhydrous phase.

3.   Results and Discussions

3.1. Structural Study

The sharp and single diffraction peaks in the XRD patterns of all the compounds, which are quite different from those of the ingredient carbonates and oxides, confirmed the formation of the new compounds. All the XRD peaks were indexed and the cell parameters were determined in different crystal systems and unit cell configurations using a standard computer program 'PowdMult' using the observed interplaner spacings (d_{obs}) of strong, medium and low intensity peaks. Finally, unit cell in cubic crystal system and cell parameter were selected for which $\Sigma\Delta d = \Sigma(d_{cal} \sim d_{obs})$ was found to be minimum. As all the members of the defect pyrochlore family have a tendency to absorb moisture from atmosphere, it can be presumed that the molybdate compounds like their tungstate counterparts are also hydrated

at room temperature. The room temperature cell parameters of the hydrated compounds are given in Table 2. Due to unavailability of previous work on these compounds in the literature, any comparison is not possible. The bulk density of the samples was determined geometrically. As the exact water content in the prepared compounds at room temperature cannot be determined, comparison of observed density with their theoretical value could not be done.

Table 1. Some preparational data of the proposed compounds

Compound Studied	Abbr. Name	Calcination Temp.(K) [Time(hr.)]	Sintering Temp.(K) [Time (hr.)]
$LiNbMoO_6$	LNM	833 [15]	913 [06]
$NaNbMoO_6$	NNM	873 [15]	893 [06]
$NaTaMOo_6$	NTM	893 [15]	953 [06]
$KNbMoO_6$	KNM	923 [15]	983 [06]
$KTaMoO_6$	KTM	783 [15]	813 [06]
$TlNbMoO_6$	TNM	1033 [15]	1133 [06]
$TlTaMoO_6$	TTM	793 [15]	853 [06]
$CsNbMoO_6$	CNM	923 [15]	973 [06]
$CsTaMoO_6$	CTM	793 [15]	823 [06]

N.B. $LiTaMoO_6$ (LTM) cannot be prepared due to its notoriously hygroscopic nature.

Table 2. Calculated cell parameters and observed density of the molybdate compounds

Compound	Calculated Cell Parameter (Å)	Observed Density (gm/cc)
LNM	10.3159	3.49
NNM	10.6505	3.26
NTM	10.5343	4.29
KNM	10.4522	3.84
KTM	10.3125	4.89
TNM	10.4891	5.37
TTM	10.9989	5.49
CNM	10.4968	4.55
CTM	10.4631	5.60

3.2.Dielectric Study

The dielectric parameters (ε, tanδ) were measured as a function of temperature (100 – 500 K) at frequencies 10^4, 10^5 and 10^6 Hz respectively. It is found that only LNM and NNM have dielectric anomaly (Table 3) in the studied frequency and temperature range. But no hysteresis loop was obtained in these compounds in spite of having dielectric anomaly. The rest of the compounds of this molybdate family do not have any such dielectric anomaly. The dielectric constant (ε) in these compounds starts increasing with temperature. The rate of

increase is more rapid in 10^4 Hz than in other two frequencies, viz., 10^5 and 10^6 Hz. In most the compounds rapid increasing trend in the values of ε is observed at temperatures ≥ 450 K. LNM has highest value of ε and tanδ among all the studied compounds (both tungstate and molybdate) of this family at 500K [10]. This type of behaviour of the compounds can be explained by their conducting nature at high temperatures. A characteristic feature of a material to become fast ion conductor / solid electrolyte is the complexity / disordering of its crystallographic structure [11]. The disordering of the cation sublattices consists of a shift of a cation from a site to one of the interstices available. Although the disordering of the sublattice as result of the movement of the cations from sites to interstices does not lead by itself to the appearance of carriers (excess carriers and their vacancies), it does facilitate substantially their formation. The reason is that the disorder is accompanied by an increase of ε and this weakens the coulomb interaction between the cation that departed to another unit cell and the vacancy that left behind. The increase of ε because of the transition of cations from sites to interstices is due to the fact that each such transition produces an equivalent dipole in the crystal whose positive charge is in the interstice and the negative charge in the site. The dipole orientation is practically arbitrary and it can orient itself with external electric field. Therefore there is an increase in the dipole moment of the system. The departure of cation to the interstice increases greatly the polarisability of the unit cell, since the length of the equivalent dipole is very large − of the order of lattice constant. The increase in the number of equivalent dipoles with rising temperature should be due to purely statistical causes, even if one disregards the interaction between them. Their number must then increases continuously with temperature and a transition from a state with low ε (ordered cation sublattice) into a state with high ε (disordered cation sublattice) occur. Therefore, a very high value of ε leads to increase in the number of carriers which in turn increases the conductivity of the compound.

The tangent loss (tanδ) of all the compounds increases with temperature. Though the tanδ values are smaller at 10^5 and 10^6 Hz compared to those at 10^4 Hz, in many compounds it could not be measured above 500K at these two frequencies. In these cases, tanδ becomes high enough and exceeds the limit of the Q-meter. High values of tanδ at temperatures ≥ 450 K can be explained by the highly conducting nature of the compounds in the above region. Addition of thermal energy increases the movement of cations in the main skeleton of the compounds − resulting in the increase of tanδ.

Table 3. Some dielectric data of molybdate compounds

Compound	Frequency (Hz)	ε at 300K	tanδ at 300K	Dielectric Anomaly (K)	ε at 500K	tanδ at 500K
LNM	10^4	14000	0.33	369	180000	8.0
	10^5	2200	0.04	370	2100	0.15
	10^6	1380	0.019	370	1200	0.028
NNM	10^4	400	0.98	364	15000	5.6
	10^5	65	0.011	365	170	0.082
	10^6	60	0.0052	365	90	0.014
NTM	10^4	27	0.13		5000	4.4
	10^5	18	0.0056	-	75	0.07
	10^6	9.8	0.0048		30	0.018
	10^4	26	0.11		4700	4.5

KNM	10^5	22	0.0078	-	80	0.20
	10^6	21	0.0054		60	0.045
KTM	10^4	29	0.25		250	2.1
	10^5	16	0.0052	-	35	0.016
	10^6	9	0.0049		22	0.0088
TNM	10^4	57	0.30		12000	3.0
	10^5	46	0.012	-	100	0.20
	10^6	37	0.0056		92	0.10
TTM	10^4	29.6	0.022		10000	4.3
	10^5	29.6	0.0060	-	100	0.10
	10^6	29.6	0.0048		45	0.016
CNM	10^4	154	0.17		39000	4.9
	10^5	130	0.0074	-	350	0.15
	10^6	118	0.0069		200	0.045
CTM	10^4	114	0.21		28000	6.6
	10^5	94	0.014	-	400	0.20
	10^6	82	0.0088		220	0.013

4. Conclusions

All the compounds of defect pyrochlore-type $ABMoO_6$ family have cubic crystal structure at room temperature. All the compounds have a tendency of absorbing moisture at room temperature which can be removed by heating the compounds. Only LNM and NNM have dielectric anomaly in the temperature range 100 – 500K. Some compounds become very lossy above 450K indicating the onset of ionic conduction in them.

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